

Study of problem of waste chemical current sources in Russia and in European countries

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Abstract. This article gives a comparative analysis of handling waste chemical current sources in Russia and in the European countries, presents the effective international documents (Directives, acts) and national legislative acts (state standards, building codes, governmental decrees, etc.), demonstrates the mechanisms for disposal and recycling of waste in the European Union countries. Along with the data of the research works, conducted in other countries during many years it presents the experimental data on leaching out heavy metals from chemical current sources by municipal solid waste landfill filtrate, depending on the morphological composition of domestic waste in the city of Irkutsk. An important point described in the article, is assessment and prediction of negative impact produced on the environment.

1. Introduction

Chemical current sources in today's world appear to be one of the most widespread industrial products in the market. The range of use of the CCS covers practically all spheres of human life: industrial, household, recreational spheres. The need to resolve the problem of WCCS disposal increases each year and is one of the most important environmental problems associated with recycling of solid municipal waste. The impact of CCS on the environment is determined first of all by the ways of their disposal. The main components contained in the CCS are heavy metals that subsequently are leached out by filtrate waters and produce a toxic effect on the environment and human health.

2. Review of literature

It is known [0] that the studies of the problems connected with the dead current sources were conducted mainly in the European countries starting from the late 1970s. This was caused by the presence in the CCS composition of mercury used to improve operating performance of the sources. At present the research works are carried out, mainly, in the countries where there are no clear rules that regulate disposal of such type of waste and Russia is one of such countries. The first stage is determination of composition of the waste and identification of its toxic components.

Depending on the operating circuit and the ability to deliver power to an electric network, chemical current sources are divided into primary, secondary and reserve types as well as electrochemical generators [[2]].



As it is known, the European laws on disposal and recycling waste batteries were adopted in 1991 (91/157 / EWG). In most of the European countries, 25-45% of all chemical current sources (CCS) are being processed, in the USA - about 60% (97% of lead-acid and 20-40% of lithium-ion batteries), in Australia - about 80% [[4]].

Directive 2008/98 / EC (Waste Management Framework Directive) presents the 5-step waste management hierarchy, according to which prevention is the most acceptable option. The programs aiming at reduction of the content of heavy metals in current sources were adopted and published in compliance with the Directive. The marking must include 2 symbols: the symbol of separate collection, presented by the Directive and a symbol indicating the content of the specific heavy metal, specified by the manufacturer.

The most comprehensive and important document in the sphere of battery disposal was the European Union Directive (2006/66/EC) of September 6, 2006 for the batteries and storage batteries and their waste products, describing in detail the measures and actions needed to reduce the content of mercury, cadmium and lead that end up in the environment.

Among the main principles that regulate disposal of waste CCS in Europe and, particularly, in Germany, are the following:

- prohibition to dump CCS without prior treatment (as follows from the Directive 1999/31/EC of April 26, 1999 on waste disposal);
- responsibility of the CCS manufacturer/importer for disposal of the goods placed in the market at the end of its life cycle;
- responsibility of municipalities for CCS collection.

Disposal of chemical current sources (CCS) by the example of Germany is regulated by the "Act regarding changes in the law on responsibility for the waste batteries and storage batteries" - BatteriesAct/BattG, adopted by the Bundestag in 2009 and by the "Rules for application of the Law on batteries and accumulators" - (BattGDV).

The activity connected with collection of small batteries in 2014 in Germany was conducted through the four systems: GRS, REBAT, ERP, Öcorecell. Over 170 000 collection points in trade outlets, waste disposal companies have been equipped with containers and transport tanks for the small batteries for the small batteries return systems. Each of the four systems for return of the waste batteries reached the minimum collection quota of 40% in 2014 and later, starting from the accounting year of 2016, this quota will have to be increased to 45% [[5], 11].



Figure 1. a) - a container for collection of CCS at the recyclable materials collection point, Dresden (Photo source: Ulanova O.) b) - containers for collection of used lithium batteries in Germany. (Photo source: Intecus GmbH).

At the stage of CCS production in the European Union, their production cost includes some percentage for their recycling wherefrom it follows that surrendering the used batteries a customer will

get a price discount when purchasing a new product. The leader in this process is Belgium, where up to 50% of batteries are sent for recycling.

All types of batteries manufactured in Europe can be processed whether or not they are rechargeable. The alkaline batteries are recycled in Great Britain, and nickel-cadmium batteries in France. About 40 enterprises in Europe are engaged in battery recycling.

For many years now in Europe, there exists the system of CCS recycling, presented on the example of Germany. The share of materials recoverable from some types of the recycled batteries attains up to 50% (without lead-acid storage batteries, where this percentage is even higher). The sale of recycled materials covers the cost of recycling the greater part of the types of batteries that, according to some estimates, ranges from 300 to 2600 Euros per ton. So far, the problem of profitability is noted mainly in recycling lithium and alkaline batteries. There is a number of waste batteries recycling technologies in the world [[6]] and different methods of recycling some battery systems applying metallurgical technologies for disposal that can be subdivided into pyrometallurgical and hydrometallurgical processes.

Management of the flow of such waste products as WCCS in the Russian Federation at present is only beginning to emerge. The present-day laws do not regulate handling of such kind of waste as the used current sources. According to the publicly available data [[3]] about 600-650 million batteries of different types are thrown out in Russia per year, and their majority (about 99%) ends up in municipal solid waste and therefrom in the landfills.

According to the Federal Supervisory Natural Resources Management Service this is the most widespread method of handling municipal solid waste in Russia, while in most cases such landfills do not meet the requirements presented to the special sites designed for the safe burial of waste. Although the share of recyclable fractions contained in solid municipal waste is quite impressive, the level of recycling in Russia according to the most optimistic estimates does not exceed 5-7%, the rest of the waste is sent to the landfills [7].

It should be noted that dead batteries (or the main types of household CCS) have not been specified as a separate type of waste in the old Federal Classificatory Catalogue of Wastes (approved on the order #786 of 02.12.2002 of the Ministry of Natural Resources and Environment, cancelled on the order #792 of 30.09.2011 of the same Ministry of the Russian Federation) or in the new FCCW introduced by the order of the Ministry of Natural Resources and Environment #445 of 18.07.2014. Such situation is explained by the small quantity of their generation in the majority of organizations, which does not permit to include the used CCS in the projects of wastes generation and disposal limits (WGDL). In cases when batteries are collected from the population separately and then surrendered to the specialized organizations that receive them for their subsequent safe storage or disposal, the collected mass of CCS are assigned group codes

Russia is only beginning to develop her civilized attitude towards collection and processing any type of waste, especially such complicated and toxic recyclable waste as the used batteries and storage batteries. Enterprises engaged in collection and recycling of the above said recyclable materials on the local level began to appear in some regions. Such companies as LLC "EkoProf" (Moscow), State Unitary Enterprise "Promotchody" ("Industrial Waste"), "HIT" ("CCS") company, LLC "Megapolisresource" (Moscow), LLC "EP Balchug" (Moscow), St. Petersburg State Unitary Enterprise "Ekostroy" (St. Petersburg), LLC "Fund" Ecology of the Don" (Rostov-on-Don) pose themselves as such that are engaged in disposal of batteries [9,10]. A number of large supermarkets (IKEA, etc.) take back the mercury lamps and used batteries from the population.

3. Materials and methods

To carry out the experimental study of the ability of leaching heavy metals into filtration water Technical University of Dresden conducted laboratory studies, modeling the processes of solid municipal waste decay in the landfill in Irkutsk.

It should be noted that the Irkutsk landfill was commissioned in 1963, its total area being 41.87 hectares. Thickness of anthropogenic sediments is about 60 m. 7 million tons of waste have been

buried on the site as of January 2015. This old landfill has an adverse impact on the environment and requires taking urgent engineering-technical measures to stop its adverse effects.

In the course of the experiment solid waste, which morphological composition corresponded to the composition of the landfill in Irkutsk, weighing 35 kg, was loaded into the reactors. Throughout the entire experiment, a constant temperature (45°C) was maintained in the bioreactors. Humidity of the waste was ensured by recirculation of the filtrate. Acceleration of the waste decay was achieved through periodic refreshing of the filtrate. The following CCS were loaded into the bioreactors: cylindrical AAA batteries ("mini") LR03, AA ("penlight") LR6, D type LR20, storage batteries (R3, R6) and flat batteries CR2016. The filtrate was sampled twice a month. Determination was made of heavy metals, pH, conductivity, redox potential, COD, BCP, sulfates, chlorides, nitrates, nitrites, ammonium ions [9].

4. Results

Analysis of the data obtained from the four bioreactors (DSR), allowed one to determine certain regularities of the leaching processes and to perform a quantitative assessment of mobilization of the heavy metals in case of CCS burial in the landfill. Analysis of the data on composition of the filtrate from the bioreactors shows relatively high content of heavy metals that stay after expiry of 3 months of the experiment.

Figure 2 shows the concentrations of Cd, Cr, Cu, Pb, Ni and Zn in the filtrate in the landfill simulation reactor during 5 weeks of the experiment.

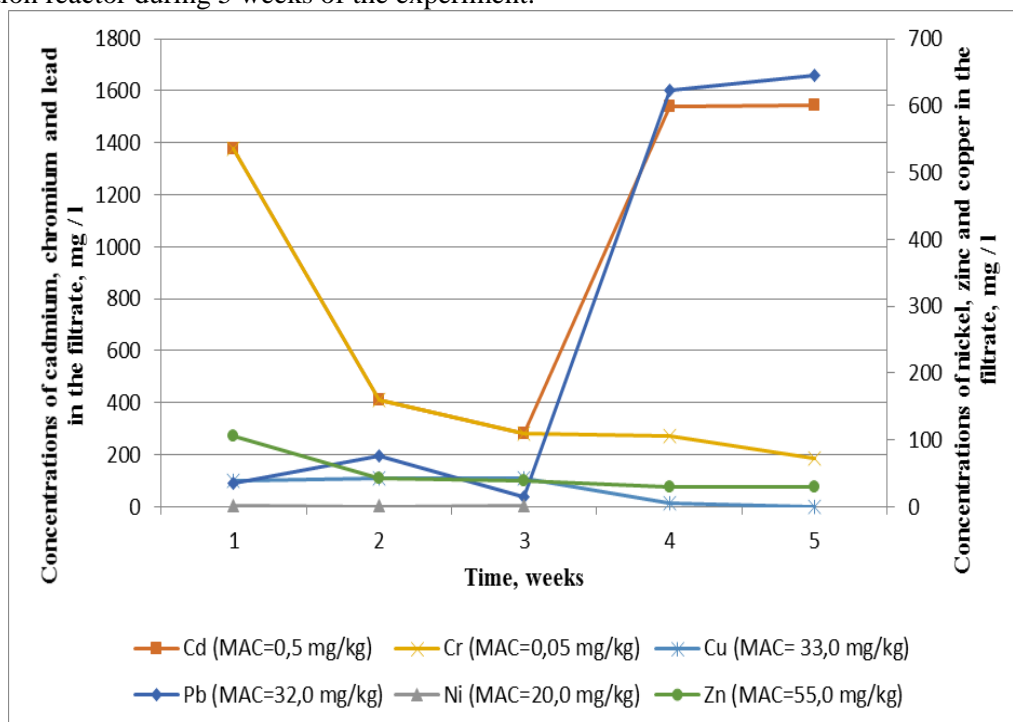


Figure 2. Graphs of changes in concentration of heavy metals in the filtrate

The studies show that Pb and Cd reach a pick of concentrations (1600-1700 mg/L) in the 5th week, which exceeds the prescribed norm for soil 53.1 and 3200 times, respectively. Concentration of nickel, copper and zinc is nearly equal to their approximate maximum permissible concentration in soil throughout the entire length of the experiment, and concentration of zinc in the first week exceeds the prescribed norm value 3.18 times with subsequent reduction within the MPC limits.

In order to assess impact produced on the environment by burial of the used current sources over the lengthy period of existence of the landfill calculation was made of the mass of heavy metals for the period of many years using data obtained in the course of the experiment and the calculation methods

[[4]]. Figure 3 shows the prediction of leaching heavy metals from CCS by MSW filtrate in Irkutsk landfill.

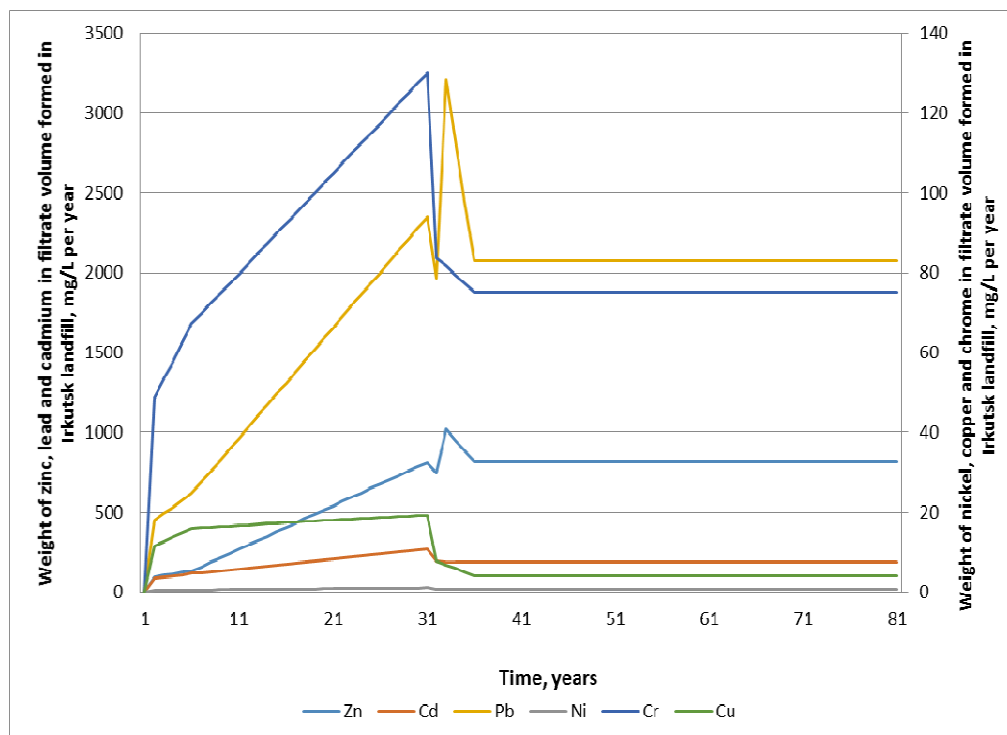


Figure 3. Prediction of leaching heavy metals from CCS by MSW filtrate in Irkutsk landfill

As can be seen from the graph dependences, there are four main elution periods. The periods of growth can be attributed to the formation of acid filtrate and annual delivery of CCS to the landfill, and periods reduced the concentration of periods to the filtrate pH. Acidic filtrate that appears to be the catalyst in the process of destruction of the battery bodies and electrolyte leaching is formed at the stage of acetogenic decomposition in the first five years of existence of the landfill. In subsequent years, the pH level increases, but due to aerobic and acetogenic decomposition of the new waste CCS concentration of metal continues to grow, but more slowly. Starting from the thirty-sixth year of existence of the landfill, accumulation of metals in landfill soil begins to take place. It should be emphasized that after closure of the landfill in the result of destruction of the overlying beds, the oxygen supply will be resumed, causing subsequent aerobic oxidation of the metals. This will result in the formation of acids reducing pH level of the eluate again and, consequently, increasing concentrations of heavy metals.

5. Discussion

Proceeding from the above said, it is possible to conclude that the burial of CCS together with solid municipal waste produces a considerable negative effect on the dumped medium by leaching out such metals as zinc, copper, cadmium, chromium, nickel and lead. Despite alkalization of the filtrate and sedimentation therein of non-ferrous metals at the stage of methanogenesis, the threat of contamination remains to be high for many years after closure of the landfill. Therefore, it is important to regulate not only the content of pollutants in the soil, but also elaborate appropriate documents (state standards, hygienic norms, building codes (GOST, HN, SNIP) for the MSW landfills in Russia.

Thus, for example, in Germany, in order to exclude the possibility of infliction of damage on the environment, back in 1993 the criteria for landfills (Table 1) have been established as part of the technical manual for municipal waste (*TASi*). The waste dumped therein must meet certain

requirements regarding their and eluate's physical and chemical characteristics, including the content of heavy metals. These days criteria presented to the waste products for their further disposal in the landfills are regulated by Regulations for landfills and long-term storage facilities (*DepV*) of April 27, 2009.

Table 1. Comparison of the values of heavy metals MPC (criteria for eluate admission to the landfill) in Germany and heavy metals MPC established for water bodies and soil in Russia

Metal	Germany			Russia	
	Technical manual for dumping waste, mg/L			MPC of chemical substances in soil.*	MPC of chemical substances in water bodies. **
	Landfill class 1	Landfill class 2	Landfill class 3		
Lead	≤0.2	≤1	≤2	32.0	0.01
Cadmium	≤0.05	≤0.1	≤0.5	6.0	0.001
Chrome VI	≤0.05	≤0.1	≤0.5	0.05	0.05
Copper	≤1	≤5	≤10	3.0	1.0
Nickel	≤0.2	≤1	≤2	4.0	0.02
Zinc	≤2	≤5	≤10	23.0	1.0

* - Hygienic Norm 2.1.7.2014-06, mg/L.

** - Hygienic Norm 2.1.7.2014-06, mg/L.

However, one cannot contend that all types of batteries are hazardous for the environment. In particular, a tripartite group of experts from Japan, the USA and Europe came to the conclusion that the alkaline batteries based on manganese and zinc-carbon batteries do not present a great danger for the environment provided that they are used and disposed of properly together with ordinary waste. Researchers at the Massachusetts Institute of Technology, who published their report in 2011 on the effects produced by alkaline batteries on the environment throughout their life cycle, arrived at about the same conclusion [9, 11].

6. Conclusion

Relying on the results of analysis of the content of heavy metals in the filtrate of Irkutsk solid municipal waste landfill, such as cadmium and lead, which concentrations exceed MPC 53.1 and 3200 times, respectively, it is possible to conclude that in 50 years of its existence, the landfill has accumulated huge amounts of hazardous waste chemical current sources so that even after its closure, the danger of leaching out the heavy metals from soil in the landfill into the environment will stay for decades. As this problem is typical for most landfills in the Russian Federation, it is necessary to not only regulate the content of pollutants in soil, but also elaborate appropriate documents (state standards, hygienic norms, building codes (GOST, HN, SNIP), establishing conditions for dumping solid municipal waste in landfills and criteria for the water filtrates of the landfills. In addition, it is necessary to establish a comprehensive system of such waste management that would include development of legislative support, separate collection, processing and a system of financing operation of those engaged in the processing work. Such mission can be also accomplished using experience of the European countries, where for many years now the mechanism for handling the waste chemical current sources exists and functions.

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